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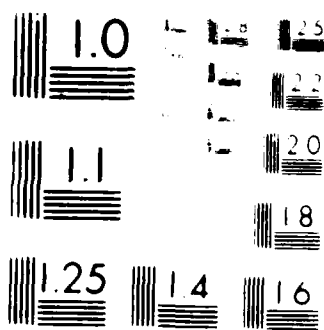
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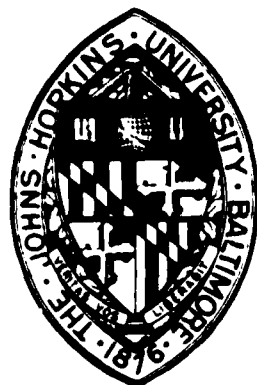
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A FUNDAMENTAL UNDERSTANDING OF THE EFFECT OF ALLOYING ELEMENTS ON THE CORROSION RESISTANCE OF RAPIDLY SOLIDIFIED Mg ALLOYS

FIRST ANNUAL REPORT
J. Kruger, G.G. Long
and D.K. Tanaka
November 26, 1986

The Johns Hopkins Univ.
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A Fundamental Understanding of the Effect of Alloying
Elements on the Corrosion Resistance of Rapidly Solidified
Mg Alloys

Jerome Kruger, Gabrielle G. Long and Deniol Tanaka

ABSTRACT

During the first year of this project progress was made in areas that bear on the effect of alloying elements on the corrosion resistance of RSP Mg alloys, theory of alloying constituents, EXAFS determination of structure of oxide or hydroxide films, and electrochemical evaluation of corrosion resistance.

The theoretical studies aided in the selection of constituents of alloying elements for binary alloys used in the complimentary Lockheed AFWAL project (Al, Ca, Zn, Li, 1%P, 1%Cr). They suggested that elements that promote hydrogen bonding in hydroxide films, Al, Zn, or B, should be beneficial. Si, which produces a surface protective SiO_2 shows promise as a alloying element.

The structural studies developed a new reflection technique (ReflEXAFS) which will enable real alloy surfaces to be studied rather than thin evaporated alloy films that simulate RSP Mg alloys as originally proposed. High quality x-ray absorption spectra have been obtained for oxide or hydroxide films on high purity Mg and alloy AZ61 as well as a MgO single crystal (for calibration purposes). The interpretation of these spectra await the completion in a few months of the development of a reflectivity model. Finally, ellipsometric measurements of the films formed on the Mg and the AZ61 indicated a thicker (and hence less effective) film forms on pure Mg.

Electrochemical polarization measurements indicate that the films on cast and RSP AZ61 are more resistant to breakdown in chloride environments than that on pure Mg. In non-chloride environments, cast AZ61 exhibits a lower passive current density (a measure of the protective quality of the passive layer) than pure Mg especially at higher pH values.

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The structural studies developed a new reflection technique (RefLEXAFS) which will enable real alloy surfaces to be studied rather than thin evaporated alloy films that simulate RSP Mg alloys as originally proposed. High quality x-ray absorption spectra have been obtained for oxide or hydroxide films on high purity Mg and alloy AZ61 as well as a MgO single crystal (for calibration purposes). The interpretation of these spectra await the completion in a few months of the development of a reflectivity model. Finally, ellipsometric measurements of the films formed on the Mg and the AZ61 indicated a thicker (and hence less effective) film forms on pure Mg.

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Introduction

This program has as its overall objective the exploitation of recently developed film characterization and corrosion resistance evaluation techniques to provide answers to the question "What is the nature of a highly effective, breakdown resistant protective oxide film on RSP Mg alloys, and how do alloying constituents control the effectiveness of such a film?"

During the first year the objectives have been: 1) a theoretical examination of how alloying constituents affect the corrosion resistant properties of the films on RSP Mg alloys and the development of a list of the most promising alloying constituents to use to provide corrosion resistant alloys for this research, 2) the development of x-ray absorption spectroscopic techniques -EXAFS (extended x-ray absorption fine structure) and XANES (x-ray absorption near edge spectroscopy) - to determine the role of alloying on the structure, composition, and electronic properties of the films on Mg alloys, and 3) the application of electrochemical and optical techniques to evaluate the corrosion behavior of Mg alloys (cast and RSP) as a function of alloy composition.

Theoretical Studies

Dr. Akos Revesz was employed as a consultant on this project to examine the role of alloying constituents on film properties and to carry out theoretical studies that would

suggest alloying constituents that show the most promise for the development of RSP alloys with improved corrosion resistance. Working with Lockheed Palo Alto Research Laboratory which is a sub-contractor on this project, he helped develop a list of binary RSP alloys (Table 1) that were selected for study by this project as well as for the complimentary AFWAL project (on which Johns Hopkins is a subcontractor).

Table 1 - Binary Alloys Proposed for Study

Mg-5%Si	Mg-10%Zn
Mg-15%Al	Mg-20%Zn
Mg-30%Al	Mg-30%Zn
Mg-45%Al	Mg-2%Li
Mg-1%Mn	Mg-8%Li
Mg-5%Mn	Mg-14%Li
Mg-5%Ca	Mg-1%P
Mg-15%Ca	Mg-1%Cr
Mg-45%Ca	

The majority of these alloys were supplied by Lockheed to Johns Hopkins for this study and the complimentary AFWAL project.

In addition to the development of a list of binary alloys for study a rough draft of paper was prepared that reviews the factors affecting the protective nature of the films that form on Mg alloys. The following points were made in this paper:

1. The ratio of molar volumes of the oxide (hydroxide) and the metal affects the protective

nature of the film (Pilling-Bedworth Rule), the ratio being 0.85 for MgO (unprotective) and 1.88 for Mg(OH)_2 (protective).

2. Films with glassy (vitreous) structures provide superior corrosion protection (1). Factors that promote more protective films are those that increase the flexibility of the structure of an oxide or hydroxide film. With regard to MgO or Mg(OH)_2 the following can be proposed:

- a) Since hydrogen bonding increases structural flexibility introducing Al, Zn or B, all of whose hydroxides possess hydrogen bonding, into a magnesium alloy could promote hydrogen bonding in Mg(OH)_2 which does not contain hydrogen bonds (2).
- b) Silicon additions to Mg can diffuse along grain boundaries to the Mg surface where it forms a vitreous protective SiO_2 layer (3).

Structural Studies

Originally it was proposed to carry out EXAFS and EXELFS (extended electron loss fine structure) studies using the thin film approach employed in past studies of iron (4). This presented the problem of having to fabricate thin Mg alloy films that were essentially the same as the RSP Mg alloys produced by more conventional techniques. One of the tasks of the first year of this project was to develop ways

to produce such thin alloy films. An opportunity, however, developed to use the soft x-ray synchrotron line belonging to SUNY-Stony Brook/BNL that enables the use of bulk alloys rather than thin films. This involved the development of a reflection technique ("ReflEXAFS") that produces EXAFS data by using total external reflection of soft x-rays near the oxygen absorption edge. This newly developed technique also eliminates the necessity to carry out EXELFS studies using an electron microscope with an electron energy loss spectrometer, to examine the oxygen edge. This is fortunate because other work during the year revealed inherent problems in the EXELFS technique. The development of the ReflEXAFS technique is especially important for the study of the oxide or hydroxide films on RSP Mg alloys because it enables a study of these films on the actual alloy surface rather than on a thin simulated alloy film or a glass substrate. This is a significant advance.

The newly developed ReflEXAFS technique is a very surface sensitive way to carry out EXAFS studies by measuring reflectance close to the angle for total reflection as a function of incident photon energy.

This technique has been employed on the U15 beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Total external reflection spectra have been measured for single crystal MgO (Fig. 1), for the oxide film on high purity Mg (Fig. 2), and for the oxide film on AZ61 alloy (Fig. 3) for numerous reflection angles. The

films on the Mg and AZ61 were formed by exposing these metals to humid air at 75°C for one hour. Ellipsometric studies of these films found that the film on the Mg was 1 nm thicker than that on the alloy AZ61, indicating a less protective layer on the Mg. Both MgO and Mg(OH)₂ have been considered as possible structures found in the passive film. Zinc is a potentially important alloying element and thus our interest in AZ61. Attempts were made to also make measurements on the surface of RSP Mg ribbon supplied by Lockheed. The ribbon was not, however, wide enough to insure the recording of a signal that did not involve contributions from the substrate to which it was attached. Efforts are now under way at Johns Hopkins by Professor Robert Pond to produce wide RSP Mg ribbons that can be measured satisfactorily.

The figures demonstrate the high quality signal-to-noise that is possible on U15 at NSLS. On the other side of the coin, the price one pays for the enhanced surface sensitivity is that the analysis is much more complex than standard absorption techniques. Such analysis is currently underway at N.B.S. and Johns-Hopkins.

Fourier transforms can be carried out on the x-ray reflection spectra given in Figs. 1,2, and 3 to provide a measure of O-O and O-Mg distances (Figs. 4-6) for a MgO single crystal (used as a calibration standard), high purity Mg, and cast AZ61, in order to compare the structures of the oxide film on pure Mg to that on an alloy. Unfortunately,

it is not yet possible to extract this structural information from Figs. 4-6 because it is necessary to develop a modeling scheme to extract absorption data from the reflectivity measurements shown in Figs. 1-3. Efforts are under way to produce such a scheme and should be completed in two months.

When these efforts are successfully completed it may be possible to extract four kinds of information on the thin oxide or hydroxide films that control the corrosion of Mg alloys:

- 1) Nearest neighbor O-O and O-Mg distances for the thin oxide or hydroxide films on Mg alloys;
- 2) The coordination numbers for the oxygen in the films;
- 3) A measure¹ of the disorder of the oxide or hydroxide in the film.
- 4) The composition of the film.

All of the above factors have been suggested by Revesz and Kruger (1) as having an important bearing on the protective ability of the films that form on an alloy; they are strongly dependent on the composition of an alloy.

In addition to the structural information than can be extracted from the ReflEXAFS technique, it is possible to gain some insight into the electronic properties of thin films or alloy surfaces -- also an important factor related

¹ A measure of the state of disorder (static not thermal disorder) can be obtained from the experimental signal $X(k)$ by fitting this signal so as to derive the amplitude reduction factor, S_0 , and the relative Debye-Waller factor, δ . The quantity $S_0 \exp(-2k^2\delta)$ is inversely proportional to the number of bonds involved - a measure of the disorder in the film on an alloy surface.

to the corrosion protective properties of these films. Such information comes from the near-edge region of an x-ray absorption (or reflection) spectrum (a technique called XANES). (This is the region a few electron volts after the absorption edge -- the sharp drop at approximately 550ev in Fig. 1). Figs. 7-9 give the derivative ($d(\text{intensity})/d(\text{energy})$) spectra for MgO and for the films on Mg and AZ61. The position of the peaks give electronic transitions but as with the Fourier transforms given in Figs. 4-6, no numbers can be extracted until the modeling scheme described earlier is developed.

ELECTROCHEMICAL STUDIES

These studies were carried out to evaluate the corrosion resistance of the alloys bearing the oxide or hydroxide films whose structural properties are being studied using the approaches described in the preceding section. These studies are complimentary to the corrosion resistance screening studies being carried out for the Lockheed AFWAL project. The electrochemical studies described here do not have screening as an object but instead seek to gain a fundamental understanding of the role of alloying on the corrosion behavior at the Mg alloys. The electrochemical studies were carried out by Gregory Makar and Dr. D.K. Tanaka.

Table 2 compares the corrosion behavior of high purity Mg, cast and RSPAZ61. It does this by listing parameters

determined from potentiodynamic polarization measurements, the passive current density, i_p , and E_{BD} , and the breakdown potential. The i_p is a measure of how effective (the lower, the more effective) the protective film on the metal surface is in controlling the corrosion in the potential regime where the metal is exhibiting its lowest rate, the passive region. E_{BD} measures the film's resistance (the higher E_{BD} is, the more breakdown resistant) to breakdown by damaging species such as chloride ions that leads to pitting or crevice corrosion. Table 2 shows that AZ61 forms a somewhat more corrosion resistant film than higher purity magnesium. The results obtained for the RSPA61 are similar to results obtained for ferrous metallic glasses. In both cases the overall corrosion rate is not particularly improved over those obtained for the cast alloy but the resistance to breakdown is improved (a higher E_{BD}). The origin of these improvements may lie in the difference in the structure of the film on the different metals which the EXAFS studies should reveal when the reflectivity modeling is completed in a few months.

Another valuable electrochemical technique for evaluating the corrosion behavior is Electrochemical Impedance Spectroscopy (EIS), also known as a.c. impedance. Figs. 10-12 show examples of the spectra obtained for high purity Mg, cast AZ61 and RSAZ61 in a borate buffer solution containing 3.5% NaCl at pH9.1. The EIS spectra are Nyquist plots in which the real part of the impedance, Z' , is

TABLE 2-- CORROSION BEHAVIOR OF HIGH PURITY Mg AND CAST AZ61
AND RSP AZ61 IN BORATE BUFFER SOLUTION WITH AND WITHOUT
3.5% NaCl

Metal	pH 9.2 no Cl ⁻ i _p ma/cm ²	pH 9.2 Cl ⁻ E _{BD} (SCE)	pH 10 no Cl ⁻ i _p	pH 10 Cl ⁻ E _{BD}
Mg	2.5	-1.55V	2.0	-1.55V
Cast AZ61	1.5		0.13	-1.48
RSP AZ61			0.4	-1.28

plotted vs. the imaginary part, $-Z''$, for different values of the frequency. The difference in the two values of the points on the x-axis where the semi-circle touches the x-axis gives a measure of the polarization, R_p , which can be used to obtain the corrosion rate of a metal in an aqueous solution. From Figs. 10-12, it can be seen that $R_p(\text{Mg}) > R_p(\text{RSAZ61}) > R_p(\text{cast AZ61})$. The larger R_p is the lower the corrosion rate. The Nyquist plots of the alloys have additional loops, which experiments producing EIS spectra at different potentials suggest are due to hydrogen.

The electrochemical experiments have thus indicated that while the pure Mg has the lowest corrosion rate, it has a lower resistance to localized corrosion (low E_{BD}) and a higher passive current density in non-chloride environments. The role played by the nature of the oxide or hydroxide film on these still preliminary results will be explored during the next year.

Future Work

Using the approaches developed during the first year and adding new techniques and studies, the following work will be carried out in the second year:

1. Complete the reflectivity modeling needed to analyze the EXAFS data,
2. Produce RSP alloy ribbons that are wide enough for the x-ray absorption spectroscopic and other techniques and

study the influence of Al, Zn and, if time permits, Si on protective film structure and corrosion resistance properties.

3. Initiate ellipsometric studies of the effect of alloying constituents on breakdown in occluded regions (e.g. crevices, cracks or pits).
4. Carry out surface analytical (scanning A.E.S. and X.P.S.) studies of films on Mg alloys. This work will be performed by Lockheed (a sub-contractor on this project) and by J.H.U. on the new surface analytical facility provided by AFOSR through a DOD equipment grant in 1986.

Summary

During the first year of this project progress was made in areas that bear on the effect of alloying elements on the corrosion resistance of RSP Mg alloys, theory of alloying constituents, EXAFS determination of structure of oxide or hydroxide films, and electrochemical evaluation of corrosion resistance.

The theoretical studies aided in the selection of constituents of alloying elements for binary alloys used in the complimentary Lockheed AFWAL project (Al, Ca, Zn, Li, 1%P, 1%Cr). They suggested that elements that promote hydrogen bonding in hydroxide films, Al, Zn, or B, should

be beneficial. Si, which produces a surface protective SiO_2 shows promise as a alloying element.

The structural studies developed a new reflection technique (ReflEXAFS) which will enable real alloy surfaces to be studied rather than thin evaporated alloy films that simulate RSP Mg alloys as originally proposed. High quality x-ray absorption spectra have been obtained for oxide or hydroxide films on high purity Mg and alloy AZ61 as well as a MgO single crystal (for calibration purposes). The interpretation of these spectra await the completion in a few months of the development of a reflectivity model. Finally, ellipsometric measurements of the films formed on the Mg and the AZ61 indicated a thicker (and hence less effective) film forms on pure Mg.

Electrochemical polarization measurements indicate that the films on cast and RSP AZ61 are more resistant to breakdown in chloride environments than that on pure Mg. In non-chloride environments, cast AZ61 exhibits a lower passive current density (a measure of the protective quality of the passive layer) than pure Mg especially at higher pH values.

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FIGURE CAPTIONS

Fig. 1. Reflectance as a function of the incident photon energy for single crystal MgO. Grazing angle of incidence is 1.7 degrees.

Fig. 2. Same as Fig. 1 for oxide film on high purity Mg. Grazing angle of incidence is 1,3 degrees.

Fig. 3. Same as Fig. 1 for oxide film on AZ61. Grazing angle of incidence is 1.7 degrees.

Fig. 4. Fourier transform of spectrum given in Fig. 1.

Fig. 5. Fourier transform of spectrum given in Fig. 2.

Fig. 6. Fourier transform of spectrum given in Fig. 3.

Fig. 7. Derivative intensity spectrum of near edge region of spectrum given in Fig. 1.

Fig. 8. Derivative intensity spectrum of near edge region of spectrum given in Fig. 2.

Fig. 9. Derivative intensity spectrum of near edge region of spectrum given in Fig. 3.

Fig. 10. Nyquist plot for high purity Mg in 0.05M sodium borate, 3.5% NaCl (pH 9.1).

Fig. 11. Same as Fig. 10 for cast AZ61.

Fig. 12. Same as Fig. 10 for RSP AZ61.

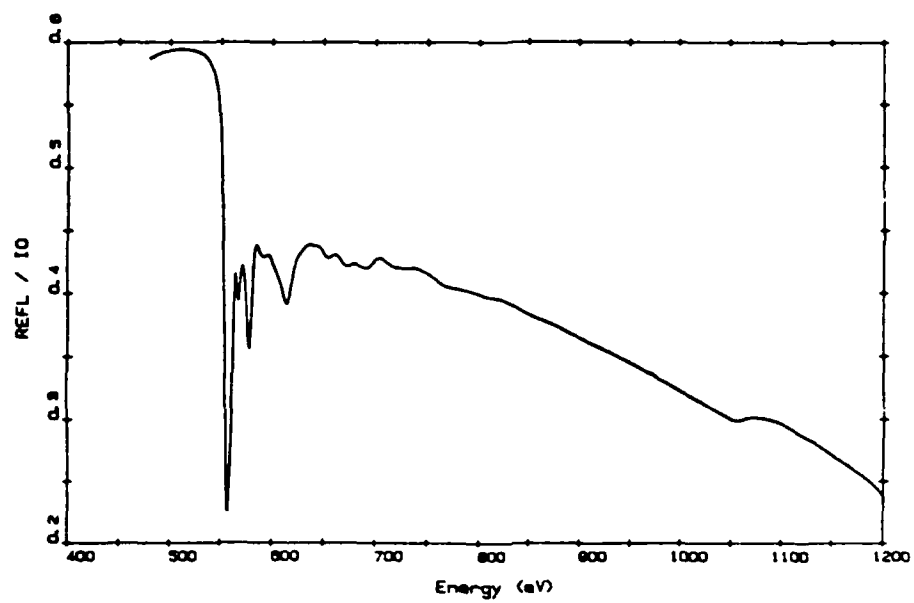


Fig. 1.

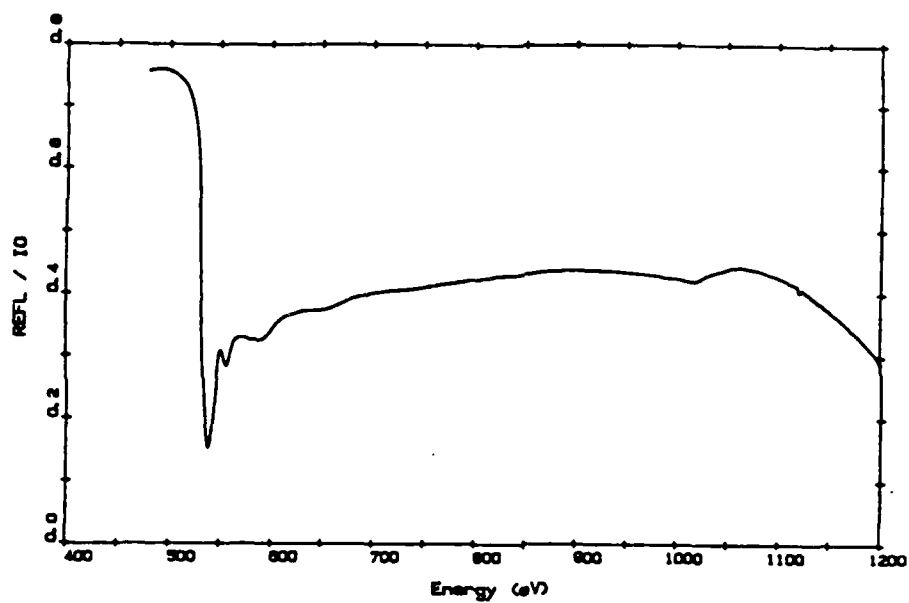


Fig. 2.

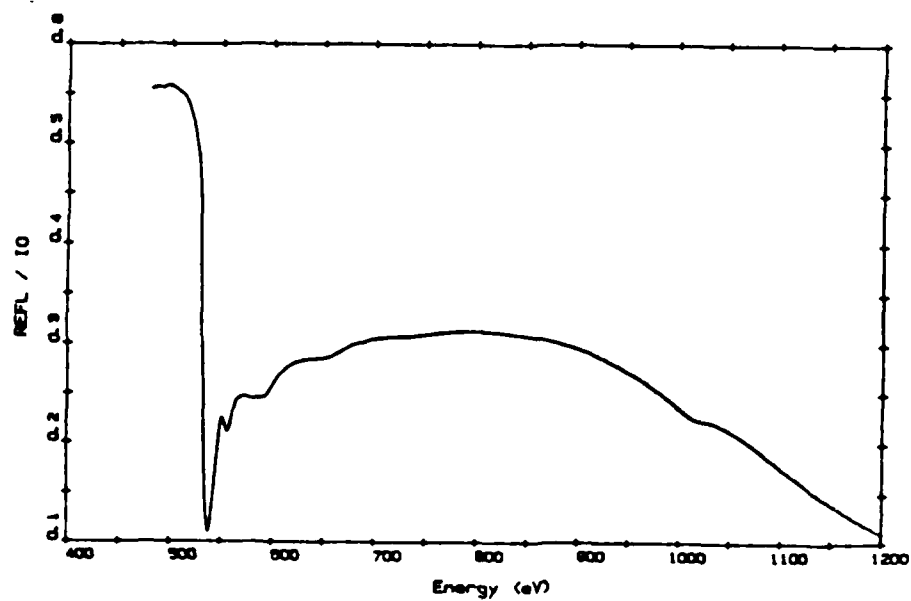


Fig. 3.

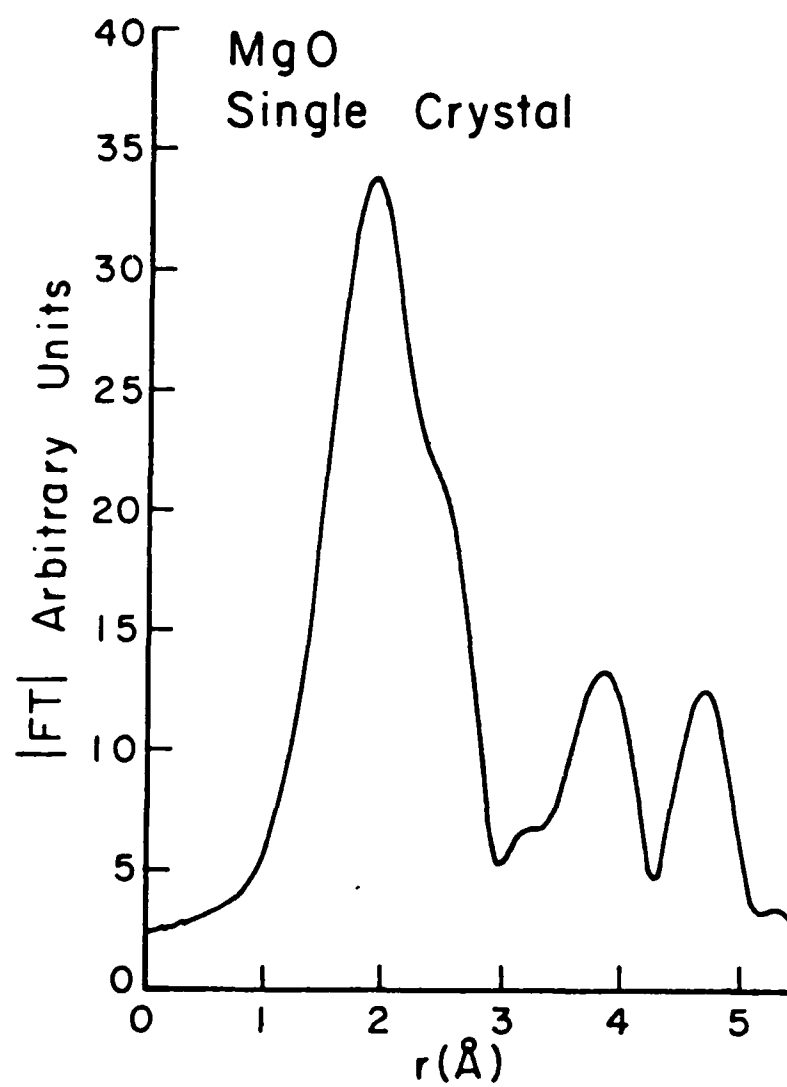


Fig. 4.

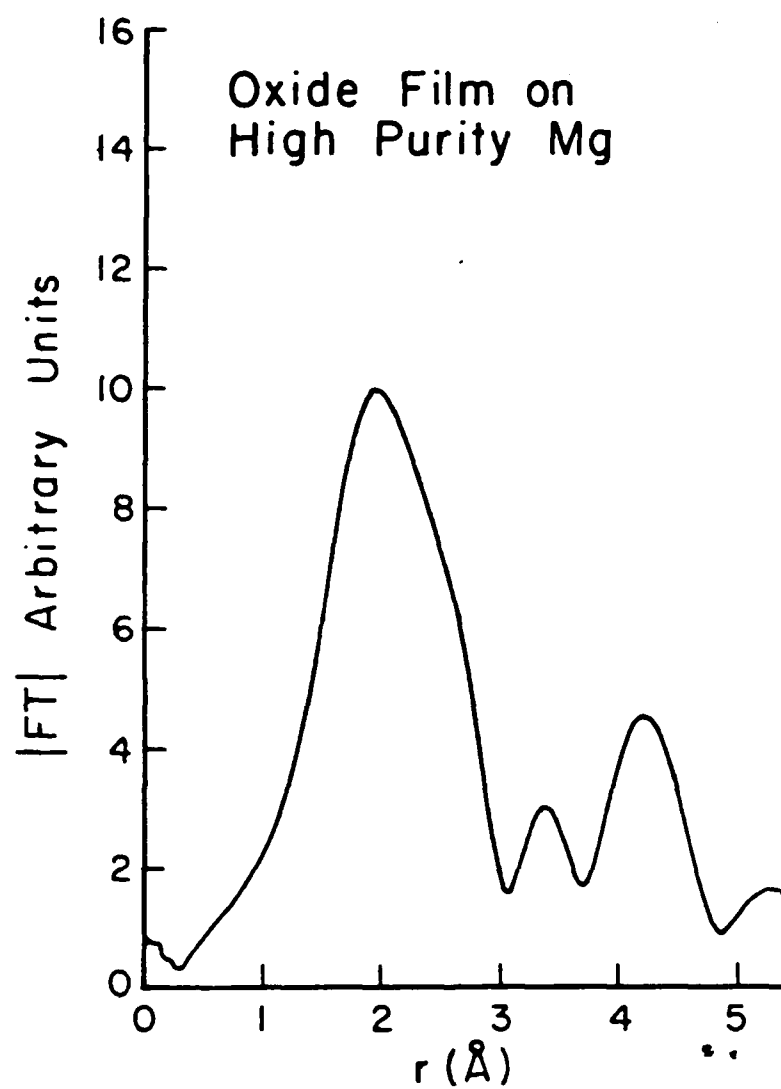


Fig. 5.

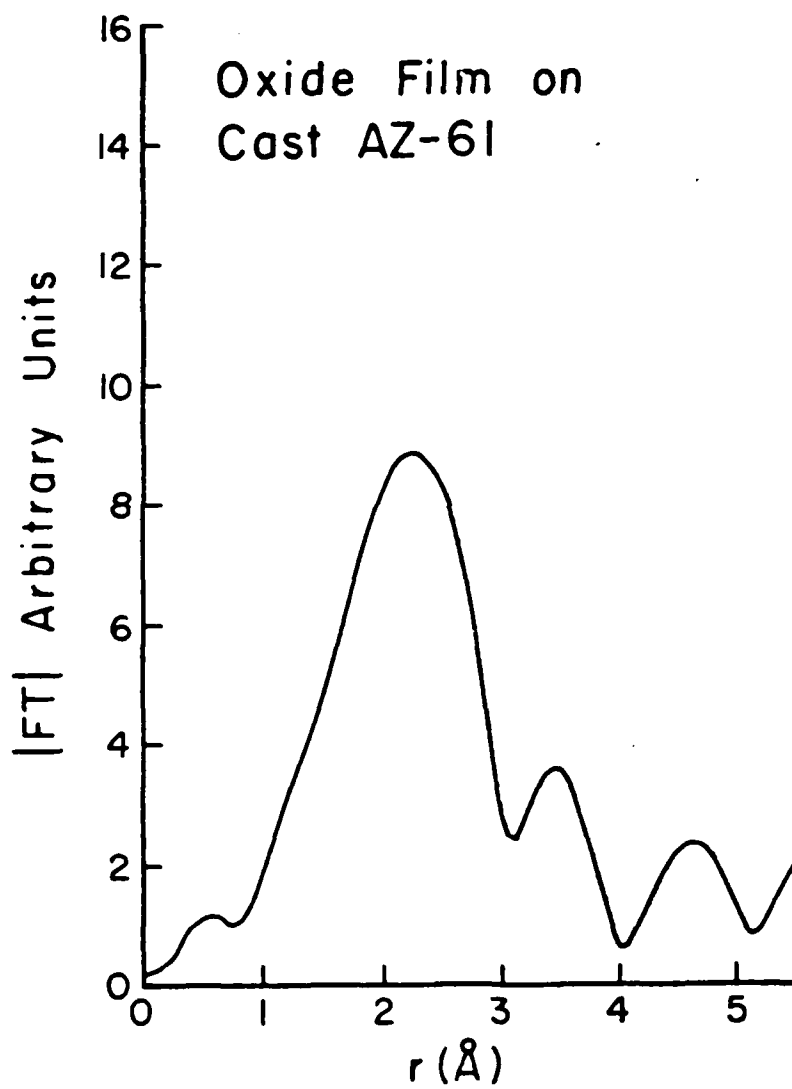


Fig. 6.

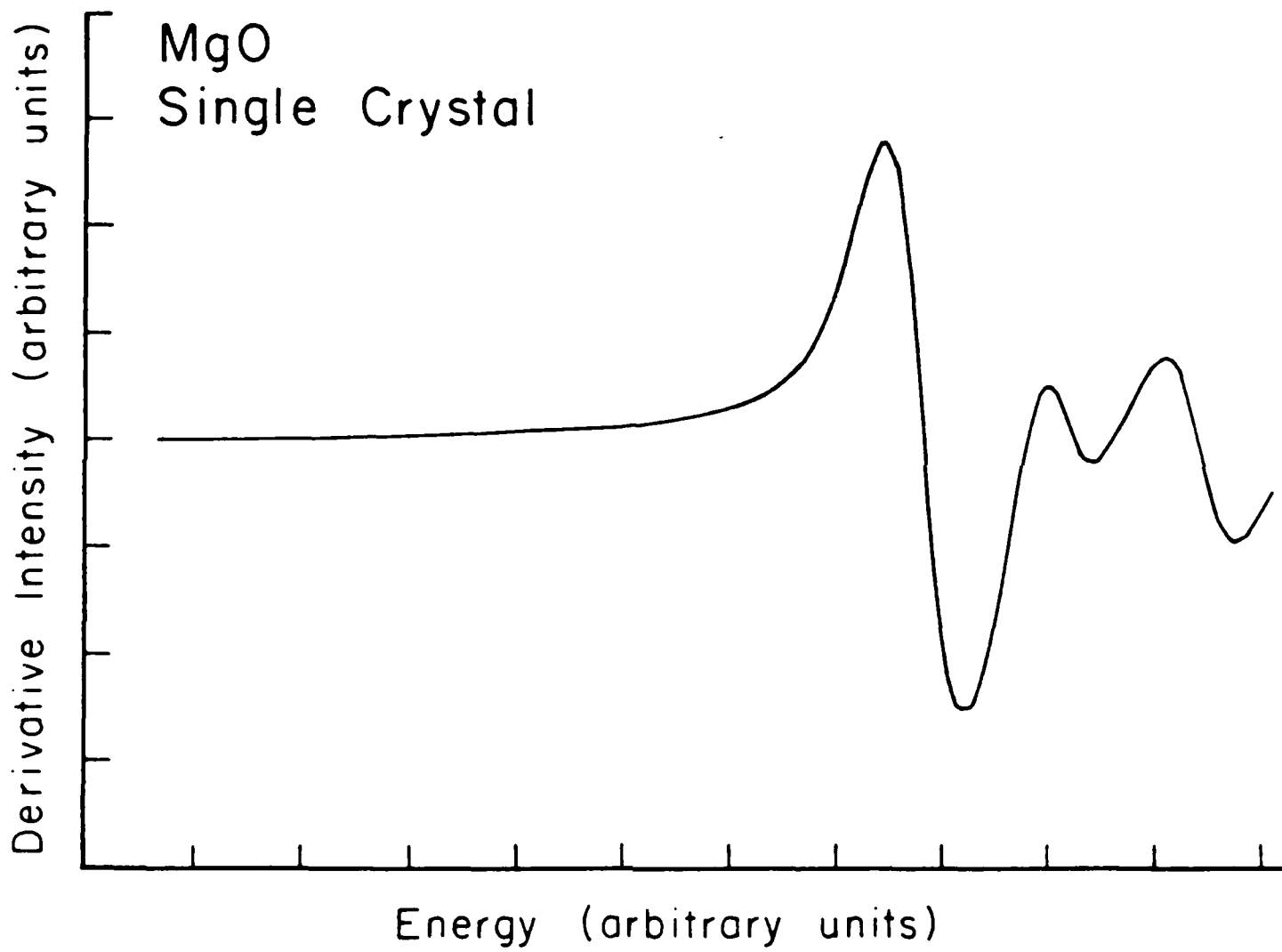


Fig. 7.

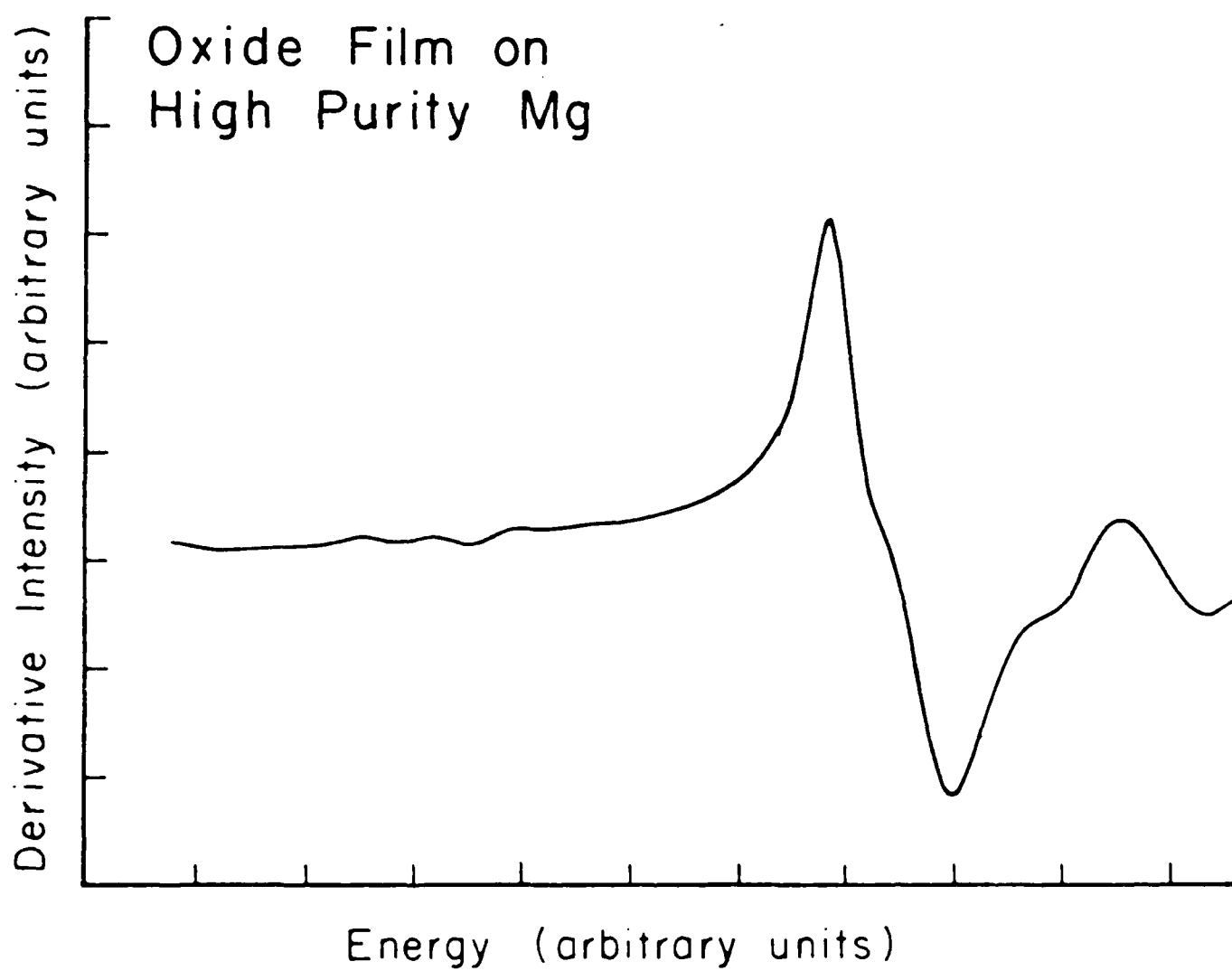


Fig. 8.

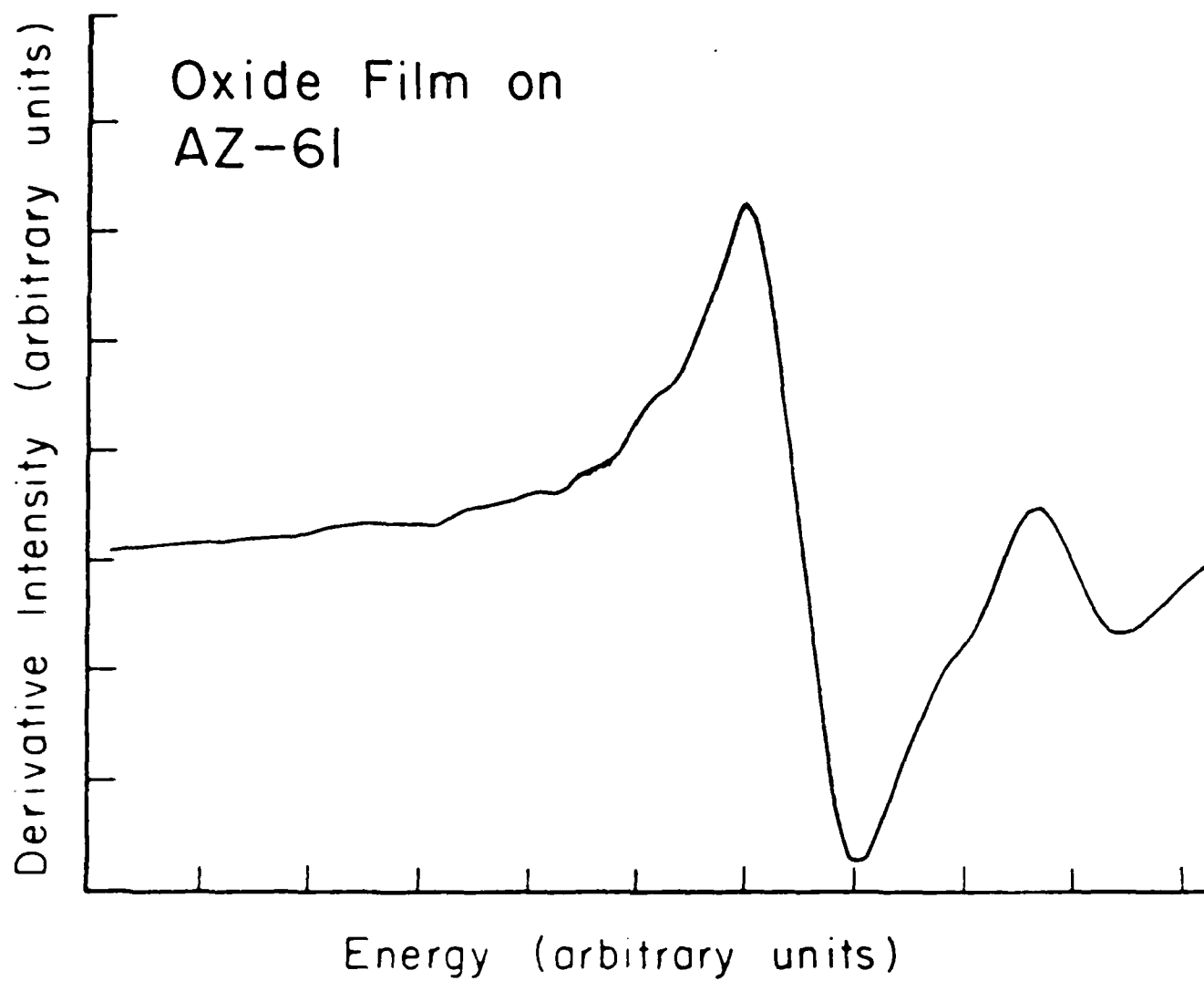


Fig. 9.

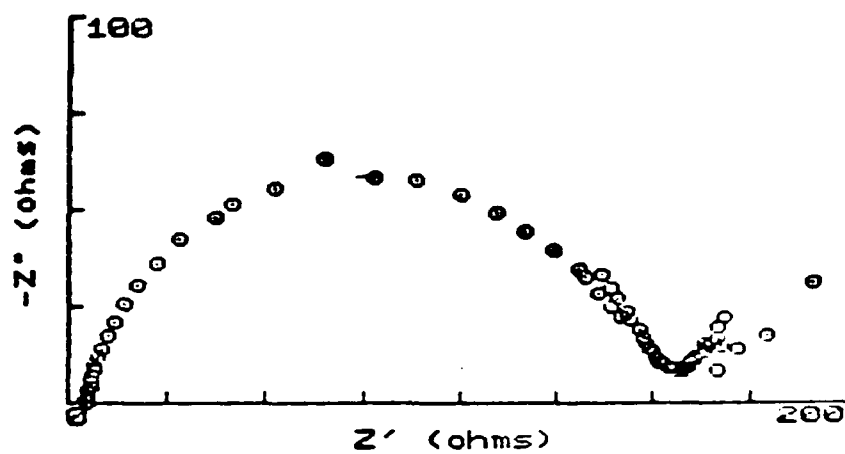


Fig. 10.

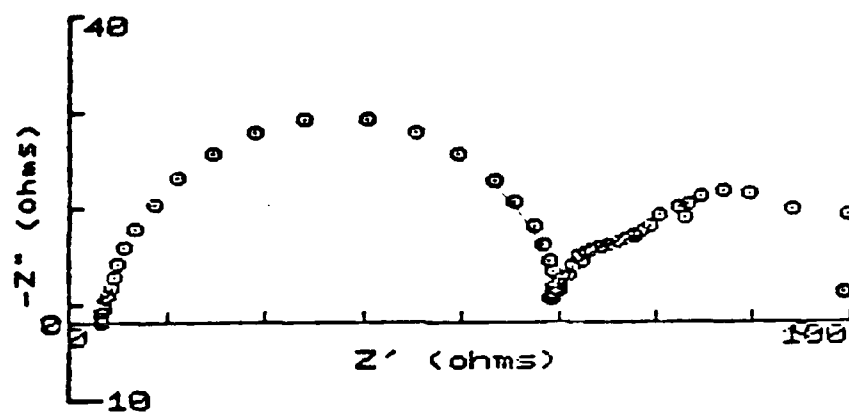


Fig. 11.

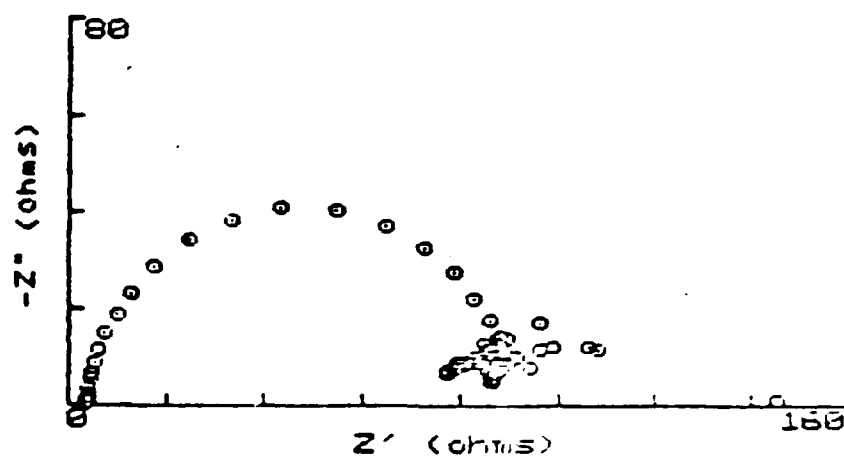


Fig. 12.

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